



VERIFICATION OF TRANSLATION

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[Document Name] Specification

[Title of the Invention] Process for Forming Semiconductor Film,
and Photoelectrode

[Claims]

5 [Claim 1] A process for forming a semiconductor film
comprising the step of applying a semiconductor particle
dispersion liquid to a surface of a substrate by spray coating in
such a manner that the atomized droplets of the dispersion liquid
discharged from the spray coater have a mean diameter of 20 μm or
10 less.

[Claim 2] The process according to claim 1, wherein the
semiconductor particle dispersion liquid is a dispersion of
titanium particles in methanol and/or ethanol.

15 [Claim 3] The process according to claim 1 or 2,
wherein the substrate is a plastic film.

[Claim 4] A semiconductor film obtained by a process
according to any one of claims 1, 2 and 3, used for photoactivity,
bacteria prevention, hydrophilization, stain prevention, anti-
fogging, gas decomposition, deodorization, water treatment, or
20 energy conversion.

[Claim 5] A photoelectrode comprising a laminate that
comprises a transparent high polymer film layer, a transparent
electrode layer, and a semiconductor film prepared by a process
according to any one of claims 1, 2 and 3.

25 [Detailed Description of the Invention]

[0001]

[Field of the Invention] The present invention relates
to a process for forming a semiconductor film that is excellent
in photoactivity, antibacterial properties, hydrophilicity, stain
30 resistance, anti-fogging properties, gas decomposing properties,
deodorizing properties, water-treating capabilities, energy
conversion properties and other properties, and a photoelectrode
prepared using the semiconductor film.

[0002]

35 [Prior Art and Problems Thereof] Semiconductor

particles such as titanium oxide have photoactivity, antibacterial properties, hydrophilicity, stain resistance, anti-fogging properties, gas decomposing properties, deodorizing properties, water-treating capabilities, energy conversion properties and other properties, and thus are used in a variety of fields. In particular, solar cells, photoelectric conversion materials, etc. are attracting attention as means for obtaining motive power, heat and other energies without adverse effects on the global environment.

10 [0003]

With regard to processes for forming a semiconductor film using particles of a semiconductor such as titanium oxide, Japanese Unexamined Patent Publication No. 1998-212120 discloses a process comprising applying a dispersion of titanium oxide particles in a solvent, such as polyethylene glycol, onto a glass, metal, ceramic or like substrate by spray coating, dip coating or like method, and then sintering the coating at 200 to 800°C.

[0004]

Further, Japanese Unexamined Patent Publication No. 2002-145615 discloses a process for forming a porous titanium oxide film on glass or like substrate, comprising intermittently spraying a starting solution containing a titanium oxide precursor, onto a substrate maintained at a high temperature so as to thermally decompose the titanium oxide precursor to titanium oxide.

[0005]

In these processes, a titanium oxide solution is sintered at a temperature of 200°C or more to form a porous titanium oxide film, and therefore they have a drawback in that they are not applicable to thermoplastic resins or like substrates (such as sheets, films, moldings, etc.) that deform or degrade at temperatures less than 200°C.

[0006]

Japanese Unexamined Patent Publication No. 1999-204152 discloses a process comprising applying a dispersion of metal

oxide particles in a high polymer material to a plastic substrate by dip coating or spray coating, and drying the dispersion at a temperature of 200°C or lower.

[0007]

5 This process employs a relatively low sintering temperature, and was developed for application to thermoplastic resin substrates. However, the metal oxide particles used in the process is a colloidal dispersion sol of a metal alkoxide, such as titanium alkoxide, and when such a sol is sprayed onto a
10 plastic sheet, the resulting titanium oxide film has good adhesion but has a small roughness factor (porosity) and inferior photoelectric conversion efficiency.

[0008]

 An object of the present invention is to provide a
15 process for forming a semiconductor film that is free from the problems of the prior art, i.e., has excellent adhesion to substrates, in particular plastic substrates, and excellent photoelectric conversion efficiency, and a photoelectrode prepared using the semiconductor film.

20 [0009]

 [Patent Document 1]

Japanese Unexamined Patent Publication No. 2002-145615

 [Patent Document 2]

Japanese Unexamined Patent publication No. 1999-204152

25 [0010]

 [Means for Solving the Problems] The present inventors found that all the problems described above can be solved by forming a semiconductor film while controlling the atomized droplets of the dispersion liquid discharged from the spray
30 coater to have a mean diameter of 20 μm or less, accomplishing the present invention.

[0011]

 The present invention provides:

 1. A process for forming a semiconductor film
35 comprising the step of applying a semiconductor particle

dispersion liquid to a surface of a substrate by spray coating in such a manner that the atomized droplets of the dispersion liquid discharged from the spray coater have a mean diameter of 20 μm or less.

5 2. The process according to item 1, wherein the semiconductor particle dispersion liquid is a dispersion of titanium particles in methanol and/or ethanol.

 3. The process according to item 1 or 2, wherein the substrate is a plastic film.

10 4. A semiconductor film obtained by a process according to any one of items 1, 2 and 3, used for photoactivity, bacteria prevention, hydrophilization, stain prevention, anti-fogging, gas decomposition, deodorization, water treatment, or energy conversion.

15 5. A photoelectrode comprising a laminate that comprises a transparent high polymer film layer, a transparent electrode layer, and a semiconductor film prepared by a process according to any one of items 1, 2 and 3.

[0012]

20 [Mode for Carrying out the Invention] The present invention is described below in detail.

[0013]

The semiconductor particle dispersion liquid for use in the process of the present invention is obtained by dispersing
25 semiconductor particles in a solvent.

[0014]

The semiconductor particles are not limited and may be any known semiconductor particles. Usable semiconductors include titanium oxide, zinc oxide, manganese oxide, cadmium oxide,
30 indium oxide, lead oxide, molybdenum oxide, tungsten oxide, antimony oxide, bismuth oxide, copper oxide, mercury oxide, silver oxide, manganese oxide, iron oxide, vanadium oxide, tin oxide, zirconium oxide, strontium oxide, gallium oxide, silicon oxide, chromium oxide and other metal oxides; SrTiO_3 , CaTiO_3 and
35 other perovskites; cadmium sulfide, zinc sulfide, indium sulfide,

lead sulfide, molybdenum sulfide, tungsten sulfide, antimony sulfide, bismuth sulfide, cadmium zinc sulfide, copper sulfide and other metal sulfides; CdSe, In_2Se_3 , WSe_2 , HgS, PbSe, CdTe and other metal chalcogenides; and GaAs, Si, Se, Cd_2P_3 , Zn_2P_3 , InP, AgBr, PbI_2 , HgI_2 , BiI_3 and other semiconductors. Also usable are composites comprising at least one member selected from the above semiconductors.

[0015]

Preferable semiconductor particles are anatase-type titanium oxide particles, which are inexpensive and has excellent performance. Commercial products of titanium oxide include "AMT-600" (tradename of TAYCA, anatase-type, mean particle size: 30 nm), "AMT-100" (tradename of TAYCA, anatase-type, mean primary particle size: 6 nm), "ST-01" (tradename of Ishihara Techno, anatase-type, mean primary particle size: 7 nm), "ST-21" (tradename of Ishihara Techno, anatase-type, mean primary particle size: 20 nm), "P-25" (tradename of Nippon Aerosil, rutile-anatase type, mean primary particle size: about 30 nm), etc.

[0016]

The mean primary particle size of the semiconductor particles is, for example, about 1 nm to about 1000 nm, and preferably about 15 nm to about 100 nm. When used for dye-sensitized solar cells (Graetzel cells), semiconductor particles with a mean primary particle size of less than 10 nm are not preferable, since the use of such particles leads to a semiconductor layer with a small mean pore size, making it difficult to transfer redox substances in the electrolyte solution and to adsorb the sensitizing dye. As a result, the current value after photoelectric conversion is low. Similarly, semiconductor particles with a mean particle size greater than 1000 nm are not preferable since use of such particles leads to a semiconductor layer that has too small a surface area to support a sufficient amount of sensitizing dye, resulting in a low current value after photoelectric conversion. Since semiconductor

particles usually aggregate into secondary particles, they are preferably dispersed using a dispersing device to obtain particles having the mean primary particle size or a mean particle size approximate to the mean primary particle size. The mean particle size of the semiconductor particles after dispersion using the dispersing device is preferably about 100 nm or less.

[0017]

Preferable solvents for dispersing the semiconductor particles include methanol and ethanol. In addition to these solvents, known organic solvents can be used, including, for example, water; xylene, toluene, and other aromatic solvents; methanol, ethanol, n-propanol, isopropanol, n-butanol, polyalkylene glycols and other alcoholic solvents; diethylene glycol, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, polyoxyalkylene glycol derivatives (e.g., polyoxyethylene(10)octylphenyl ether) and other ethereal solvents; acetone, methyl ethyl ketone and other ketonic solvents; methyl acetate, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate and other ester solvents; etc.

[0018]

The dispersion liquid may contain, in addition to the above materials, known complexing agents (e.g., acetyl acetone), dispersing resins, etc.

[0019]

The substrate for use in the process of the present invention is not limited and may be selected from various known substrates. Specifically, usable substrates include plastics, glass, metals, concretes, coating films, etc., among which plastics are preferable in the present invention. Preferable examples of plastics include polyethylene terephthalate, silicon resins, fluororesins, acrylic resins, etc. From the viewpoint of practical use, polyethylene terephthalate is particularly preferable.

[0020]

The semiconductor particle dispersion liquid for use in the present invention preferably has a solids content of about 1 wt.% to about 40 wt.%, and preferably about 5 to about 30 wt.%,
5 at the time of spray coating. When the dispersion liquid has a solids content less than 1 wt.%, it is difficult to obtain the necessary film thickness, with the result that the obtained semiconductor film is liable to have insufficient photoelectric conversion efficiency. Moreover, with such a solids content, the
10 dispersion liquid as deposited is unlikely to have an adequate solids content (usually 90 wt.% or more) controlled by spray coating, which is a feature of the present invention. This makes it difficult to obtain a thin semiconductor film that is porous and has good adhesion.

15 When the dispersion liquid has a solids content of more than 40 wt.%, the mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is large, and a semiconductor film with excellent photoelectric conversion efficiency cannot be obtained. Moreover, when the dispersion
20 liquid has a high solids content, the movement of the semiconductor particles in the atomized droplets of the dispersion liquid is restricted, resulting in that the semiconductor particle binding energy, which is a feature of the present invention, produced by the sharp decrease of the kinetic
25 energy of the semiconductor particles from the start of the spraying of the dispersion liquid until the deposition on the substrate, is reduced. Thus, it becomes difficult to obtain a thin semiconductor film with good adhesion and high strength.

[0021]

30 The dispersion liquid to be applied by spray coating preferably has a viscosity of 0.001 Pa·sec to 1 Pa·sec, and more preferably 0.001 Pa·sec to 0.1 Pa·sec. When the viscosity is less than 0.001 Pa·sec, the dispersion liquid is imparted with only a low energy by spraying, and therefore the semiconductor particles
35 have a low initial energy, making it difficult to obtain a thin

semiconductor film with good adhesion. When the dispersion liquid has a viscosity of more than 1 Pa·sec, atomization of the dispersion liquid into droplets, which is a feature of the present invention, is difficult, and a thin semiconductor film
5 with good adhesion cannot be obtained.

[0022]

Examples of spray coaters usable in the process of the present invention include electrostatic spray coaters, non-electrostatic spray coaters, rotary spray coaters, magnetic spray
10 coaters, ultrasonic atomizers and other known spray coaters. Electrostatic spray coaters and ultrasonic atomizers are particularly preferable. Preferably usable nozzles include two-fluid spray nozzles that can form atomized droplets with a narrow particle size distribution.

15 [0023]

Optimal spraying conditions for such spray coaters, such as nozzle type, atomization air pressure, pattern width, discharge amount, discharge pressure, coating speed, number of stages (number of coating applications), nozzle-substrate
20 distance, etc., vary depending on the type of the coater used, and thus suitable conditions are selected according to the type of coater to be used, so that the atomized droplets of the dispersion liquid discharged from the spray coater has a mean diameter of 20 μm or less, preferably 1 to 20 μm , and more
25 preferably 1 to 15 μm . When the atomized droplets of the dispersion liquid have a mean diameter of more than 20 μm , it is likely that the dispersed particles clog the nozzle tip or that the atomized droplets of the dispersion liquid deposited on the substrate surface unevenly agglomerate, leading to a small
30 roughness factor. As a result, it is difficult to obtain a semiconductor film with good adhesion to the substrate and high photoelectric conversion efficiency. Further, when the atomized droplets of the dispersion liquid have a large mean diameter, the solvent volatilizes only slowly, and thus the dispersion liquid
35 deposited on the substrate has a low solids content, failing to

attain sharp decrease of the kinetic energy of the semiconductor particles in the atomized droplets, which is a feature of the present invention. Thus, sufficient binding energy cannot be obtained.

5 [0024]

Examples of suitable coating conditions are as follows: an atomization air pressure of 0.5 to 5.0 kgf/cm² and preferably 1.0 to 3.0 kgf/cm²; a discharge amount of 1 to 500 g/min and preferably 10 to 100 g/min; a nozzle-substrate distance of 5 to 10 100 cm and preferably 10 to 50 cm; a coating speed of 1 to 200 m/min and preferably 10 to 100 m/min; a coating pitch of 5 to 100 mm and preferably 10 to 30 mm; a stage number of 1 to 100 and preferably 1 to 10.

[0025]

15 In this specification and the appended claims, the mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is measured using a "2600 Particle Sizer" (tradename of Malvern). For the measurement, it is aligned to the center portion of the spray from the side of 20 the spray gun, and the distance from the nozzle tip to the substrate was the same as in actual coating operation.

[0026]

The semiconductor particle dispersion liquid is applied to a substrate and heated or dried at room temperature to form a 25 semiconductor film. Heating conditions can be suitably selected according to the type of substrate. Specifically, for example, when using a glass plate, baking can be performed at a temperature of 300°C or higher. When using a plastic (polyethylene terephthalate), baking can be performed at a 30 temperature of 200°C or lower, and more preferably 150°C to 180°C.

[0027]

In the process of the present invention, the thickness of the semiconductor film can be suitably selected according to the intended use, and is usually 1 μm to 100 μm, and preferably 2 35 μm to 50 μm.

[0028]

Many of semiconductor films formed according to the process of the present invention are activated by light irradiation, and thus can be used in known applications utilizing such a property, including, for example, photoactivity, bacteria prevention, hydrophilization, stain prevention, anti-fogging, gas decomposition, deodorization, water treatment, and energy conversion.

[0029]

10 Photoelectrodes for dye-sensitized solar cells are described below as an example of application of the semiconductor film according to the present invention.

[0030]

15 Generally, a dye-sensitized solar cell comprises a photoelectrode comprising a transparent substrate (e.g., a glass plate or plastic sheet) provided on one side with an electrically conductive transparent layer (electrode) and semiconductor layer; a counter electrode facing the semiconductor layer; and an electrolyte layer sandwiched between the electrodes.

20 [0031]

The semiconductor layer is usually made of semiconductor particles, has pores, and supports a photosensitizing dye on the particle surfaces or in the pores.

[0032]

25 The electrically conductive transparent layer is formed on the surface of a glass plate, a plastic sheet or like transparent substrate by vapor-depositing gold, silver, aluminum, indium, indium tin oxide (ITO), tin oxide or the like.

[0033]

30 The semiconductor film formed by the process of the present invention can be used as the semiconductor layer. The semiconductor layer is usually 1 μm to 100 μm thick, and preferably 2 μm to 50 μm thick.

[0034]

35 The photosensitizing dye can be selected from various

known dyes that absorb light in the visible region and/or the infrared region of the spectrum.

[0035]

Examples of photosensitizing dyes include azo dyes,
5 quinone dyes, quinoneimine dyes, quinacridone dyes, squarylium
dyes, cyanine dyes, merocyanine dyes, triphenylmethane dyes,
xanthene dyes, porphyrin dyes, phthalocyanine dyes, perylene dyes,
indigo dyes, naphthalocyanine dyes, etc. Among these, metal
complex dyes, such as phthalocyanine dyes and naphthalocyanine
10 dyes, have a high quantum yield and high durability against light,
and therefore are preferable as photoelectric conversion
materials.

[0036]

Examples of metals to be combined with the
15 photosensitizing dye include copper, nickel, iron, cobalt,
vanadium, tin, silicon, titanium, germanium, cobalt, zinc,
ruthenium, magnesium, aluminum, lead, manganese, indium,
molybdenum, zirconium, antimony, tungsten, platinum, bismuth,
selenium, silver, cadmium, platinum, etc. Among these, copper,
20 titanium, zinc, aluminum, iron, vanadium and silicon are
preferable since metal complex dyes comprising these metals have
a high quantum efficiency.

[0037]

The amount of the photosensitizing dye to be supported
25 by the semiconductor particles is preferably 10^{-8} mol/cm² to 10^{-6}
mol/cm², and more preferably about 0.1 to 9.0×10^{-7} mol/cm². Less
than 10^{-8} mol/cm² of photosensitizing dye does not sufficiently
improve the photoelectric conversion efficiency. More than 10^{-6}
mol/cm² of photosensitizing dye does not further improve the
30 photoelectric conversion efficiency, and is uneconomical.

[0038]

The electrolyte used in the electrolyte layer is not
limited as long as it comprises a redox pair in a solvent.
Preferably, the redox pair consists of an oxidant and reductant
35 with the same electric charge. The redox pair is a pair of

substances that reversibly exist in an oxidized or reduced form in an oxidation-reduction reaction system. Redox pairs are well known to persons of ordinary skill in the art. Examples of redox pairs include chlorine compound-chlorine, iodine compound-iodine, 5 bromine compound-bromine, thallium ion (III)-thallium ion (I), mercury ion (II)-mercury ion (I), ruthenium ion (III)-ruthenium ion (II), copper ion (II)-copper ion (I), iron ion (III)-iron ion (II), vanadium ion (III)-vanadium ion (II), manganic acid ion-permanganic acid ion, ferricyanide-ferrocyanide, quinone-10 hydroquinone, fumaric acid-succinic acid, etc. Other redox pairs are also of course usable. Among the above redox pairs, iodine compound-iodine is preferable. Preferable iodine compounds include lithium iodide, potassium iodide and other metal iodides; tetraalkylammonium iodine, pyridinium iodine and other quaternary15 ammonium iodide salt compounds; dimethylpropylimidazolium iodide and other diimidazolium iodide compounds; etc.

[0039]

The solvent to be used for dissolving the electrolyte is preferably a compound that dissolves the redox pair and has 20 high ionic conductivity. An aqueous solvent and/or organic solvent can be used, and an organic solvent is preferable to better stabilize the redox pair. Specific examples of organic solvents include dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, ethylene carbonate, propylene carbonate and 25 other carbonate compounds; methyl acetate, methyl propionate, γ -butyrolactone and other ester compounds; diethyl ether, 1,2-dimethoxyethane, 1,3-dioxolane, tetrahydrofuran, 2-methyltetrahydrofuran and other ether compounds; 3-methyl-2-oxazolidine, 2-methylpyrrolidone and other heterocyclic 30 compounds; acetonitrile, methoxyacetonitrile, propionitrile and other nitrile compounds; sulfolane, dimethylsulfoxide, dimethylformamide and other aprotic polar compounds; etc. Such solvents may be used singly or in combination. Especially preferable solvents include ethylene carbonate, propylene 35 carbonate and other carbonate compounds; 3-methyl-2-oxazolidine,

2-methylpyrrolidone and other heterocyclic compounds; and acetonitrile, methoxyacetonitrile, propionitrile and other nitrile compounds.

[0040]

5 The electrolyte may be in the form of a liquid, solid or gel.

[0041]

[Effects of the Invention] The process of the present invention, in which a semiconductor particle dispersion liquid is
10 applied by spray coating in such a manner that the atomized droplets of the dispersion liquid have a mean diameter of about 20 μm or less, has the following remarkable advantages:

[0042]

1. When the semiconductor particle dispersion liquid
15 applied to a substrate, the semiconductor particles or small aggregates thereof form a semiconductor film, and thus the film is porous and has excellent adhesion to the substrate.

[0043]

2. In particular when ethanol is used as a solvent in
20 the semiconductor particle dispersion liquid, the dispersion liquid is stable because of the high affinity of ethanol to the semiconductor particles. Therefore, the dispersion liquid, even when being subjected to a high shear stress at the time of spray coating, is unlikely to cohere at the nozzle tip and thereby clog
25 the nozzle.

[0044]

3. Part of ethanol evaporates from the dispersion liquid during spray coating, the semiconductor particles being sprayed are stabilized.

30 [0045]

4. The high affinity of ethanol facilitates necking of the particles of the semiconductor particle dispersion liquid, and thus even when the dispersion liquid is applied to a flexible substrate such as a plastic film, it does not peel off when the
35 substrate flexes.

[0046]

5. In prior art techniques, a semiconductor particle dispersion liquid is applied to a glass plate or like substrate, and sintered at 200°C or higher to form a porous semiconductor film. In contrast, the process of the present invention is capable of forming a porous semiconductor film at low temperatures, and therefore can be applied to a plastic film or like substrate.

[0047]

[Examples] The following Examples are given to illustrate the present invention in further detail. In these examples, parts and percentages are all by weight.

[0048]

Production Example of Titanium Oxide Particle Sol

Thirty parts of "P-25" (tradename of Japan Aerosil Co., Ltd., rutile-anatase-type titanium oxide (TiO_2) crystals, mean primary particle size: 30 nm) and 120 parts of ethanol were dispersed using glass beads in a paint shaker for 6 hours, to thereby obtain a titanium oxide sol.

[0049]

Example 1

A polyethylene terephthalate (PET) sheet was spray-coated with the above titanium oxide sol under the coating conditions presented in Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is shown in Table 1.

The resulting coating was dried by heating at 150°C for 30 minutes, to thereby obtain a 8 μm thick titanium oxide film.

[0050]

Table 2 shows the adhesion and scratch resistance of the obtained titanium oxide film.

[0051]

The titanium oxide sol was applied to an electrically conductive PET (ITO) under the conditions shown in Table 1, and baked at 150°C for 30 minutes to obtain a 8 μm thick porous

titanium oxide film. The porous film was immersed at room temperature overnight in an ethanol solution containing a sensitizing dye [Ru(2,2'-bipyridil-4,4'-dicarboxylate(TBA))₂(NCS)] at a concentration of 5×10^{-4} M/L. The
5 above-mentioned electrically conductive PET film sputtered with platinum was superimposed as the counter electrode on the sensitizing dye-adsorbing porous titanium oxide film. An electrolyte solution (40 mM iodine, 500 mM tetrapropylammonium iodine, 80 M ethylene carbonate and 20 M acetonitrile) was poured
10 to obtain a dye-sensitized solar cell. Table 2 shows the photoelectric conversion efficiency of the cell.

[0052]

Example 2

Spray coating was performed under the coating
15 conditions shown in Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater is shown in Table 1.

[0053]

The coating was dried by heating at 150°C for 30
20 minutes to thereby obtain a 12 μ m thick titanium oxide film.

[0054]

Table 2 shows the adhesion and scratch resistance of the obtained titanium oxide film.

[0055]

25 A dye-sensitized solar cell was obtained in the same manner as in Example 1 except for employing the coating conditions shown in Table 1. Table 2 shows the photoelectric efficiency of the cell.

[0056]

30 Comparative Example 1

The titanium oxide sol was applied with a knife coater and dried by heating at 150°C for 30 minutes to thereby obtain a 8 μ m thick titanium oxide film.

[0057]

35 Table 2 shows the adhesion and scratch resistance of

the obtained titanium oxide film.

[0058]

Comparative Example 2

5 Spray coating was carried out under the conditions
shown in Table 1. The mean diameter of the atomized droplets of
the dispersion liquid discharged from the spray coater is shown
in Table 1.

[0059]

10 The resulting coating was dried at 150°C for 30 minutes
to thereby obtain a 8 μm thick titanium oxide film.

[0060]

Table 2 shows the adhesion and scratch resistance of
the obtained titanium oxide film.

[0061]

15 Test methods

Photoelectric conversion efficiency (%): Measured using
an artificial sunlight (xenon lamp) (JIS A.M.1.5, unit: 100
 mW/cm^2).

[0062]

20 Adhesion: A porous film that did not peel off even when
the PET film with the porous film formed thereon was sharply bent
or forcefully hit was evaluated as having good adhesion, while a
porous film that peeled off when the PET film with the porous
film was bent was evaluated as having poor adhesion.

25 [0063]

Film scratch resistance (film strength): Titanium oxide
films were formed in the same manner as in the Examples and
Comparative Examples except for using, as the substrate, a glass
plate in place of the PET film, and used as test samples.

30 [0064]

Using a "Tribogear Type 18L" (tradename of Shinto
Scientific Co., Ltd.), the load at which the glass plate was
uncovered was found by applying a vertical load of 0 to 100 g to
a scratch needle (made of sapphire, 1.2 mm in diameter) and
35 moving the needle at a rate of 600 mm/min over a distance of 100

mm. The greater the load, the higher the scratch resistance. A load of 10 gf or more is particularly preferable.

[0065]

[Table 1]

5 Table 1

	Discharg- ed amount (g/min)	Atomization air pressure (kgf/cm ²)	Number of Stages	Nozzle- substrate distance (mm)	Coating rate (m/min)	Cover- ing Pitch (mm)	Mean diam- eter (μm)	Film thick- ness (μm)
Ex.1	60	3.0	3	20	60	15	19.7	8
Ex.2	60	2.0	3	20	60	15	24.3	9
Comp. Ex.2	60	1.0	3	20	60	15	41.4	10

[0066]

[Table 2]

Table 2

	Conversion efficiency	Adhesion	Scratch resistance
	(%)		(gf)
Ex. 1	2.1	Good	14.1
Ex. 2	1.6	Good	12.6
Comp.Ex. 1	-	Poor	6.1
Comp.Ex. 2	-	Poor	7.3

[Document Name] Abstract

[Abstract]

[Objects] To provide a process for forming a semiconductor film, and a photoelectrode.

- 5 [Means for Achieving the Objects] A process for forming a semiconductor film, comprising the step of applying a semiconductor particle dispersion liquid, which is a dispersion of titanium particles in methanol and/or ethanol, to a substrate surface by spray coating in such a manner that the atomized
- 10 droplets of the dispersion liquid discharged from the spray coater have a mean diameter of 20 μm or less; and a semiconductor film obtained by the process and used for photoactivity, bacteria prevention, hydrophilization, stain prevention, anti-fogging, gas decomposition, deodorization, water treatment, or energy
- 15 conversion; and a photoelectrode comprising a laminate that comprises a transparent high polymer film layer, transparent electrode layer and a semiconductor film obtained by the above process for forming a semiconductor film.

[Selected Figure] None.